A NEW APPROACH TO "HIGH SOLIDS" SAMPLE

INTRODUCTION FOR FLAME ATOMIC ABSORPTION ANALYSIS

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Studies are presented describing direct, clog-free production of high density finely dispersed aerosols from highly complex samples through use of a special nebulizer design based on principles first developed by R. S. Babington. Application of this technique to sample introduction for atomic absorption spectrometry is described for matrices of combined high suspended solids content, increased viscosity, and elevated salt concentration. Cu and Zn are determined in whole blood, urine, sea water, evaporated milk concentrate, and tomato sauce with minimal sample preparation.

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A NEW APPROACH TO "HIGH SOLIDS" SAMPLE

INTRODUCTION FOR FLAME ATOMIC ABSORPTION ANALYSIS

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CREDIT

BRIEF

Development of a new clog-free Babington principle nebulizer is reported for direct flame spectrochemical analysis of a variety of highly complex materials such as tomato sauce and whole blood.

TITLE

A New Approach to "High Solids" Sample
Introduction for Flame Atomic Absorption Analysis

ABSTRACT

Studies are presented describing direct, clog-free production of high density finely dispersed aerosols from highly complex samples through use of a special nebulizer design based on principles first developed by R. S. Babington. Application of this technique to sample introduction for atomic absorption spectrometry is described for matrices of combined high suspended solids content, increased viscosity, and elevated salt concentration. Cu and Zn are determined in whole blood, urine, sea water, evaporated milk concentrate, and tomato sauce with minimal sample preparation.

INTRODUCTION

Increasingly large numbers of environmental and clinical samples being submitted to analytical laboratories for determination of trace metal constituents make the development of "preparation free" methods of analysis extremely important from the standpoint of cost per analysis, speed, convenience, and freedom from reagent contamination. Atomic absorption spectrometry has been widely applied to samples of complex nature directly (1), and indirectly through the use of digestion (2) and extraction procedures (3). Although such digestion or separation procedures tend to be time-consuming and may frequently lead to volatilization loss (2) or sample contamination, existing methods often require these steps for a wide variety of samples. The complexity of untreated matrix that may be introduced directly is often limited by non-atomic absorption and vaporization interferences in the case of flameless sampling devices, and by clogging of the capillary orifice and burner slot in the case of conventional burner-nebulizer systems.

Although less sensitive than flameless atomizers, conventional burner-nebulizers have proven to be generally more convenient to operate, lower in cost, capable of introducing a larger number of samples per unit time into the absorption cell, and less susceptible to interferences (4,5). These advantages have established the continued use of the capillary pneumatic nebulizer as a principal sample introduction device for analytical atomic spectroscopy. Culver (6) has discussed the relative merits of carbon rod and flame techniques and concludes that, although flameless atomizers provide an alternative to nebulizer-burner atomization cells when greater

sensitivity and smaller sample size is required, the more convenient flame system should be used whenever possible. Improvement in nebulizer design to allow more complex sampling is therefore highly relevant and desirable.

Development and subsequent characterization of a unique nebulization principle by R. S. Babington (7) have resulted in the ability to generate high density, finely dispersed aerosols directly from a variety of extremely complex materials including fuel oil, paints, food products, etc. Possibilities for improved freeze-drying systems, oil burners for home heating, insecticide fogging, etc., applications have been outlined (8). A nebulizer based on this principle has been marketed by Owens-Illinois (Toledo, Ohio) and more recently by McGaw Respiratroy Therapy (Irvine, Calif.) under the trade names of "HYDROSHPERE" and "MAXI-COOL" for the production of aerosols utilized in respiratory inhalation therapy. This Babington nebulizer has been reported to produce a dense aerosol with a droplet distribution (following considerable aerosol refinement) of median mass diameter at 3.6 microns with 95% of all refined droplets being below 5 microns in diameter (9). In view of the spectrochemical importance of droplet size discussed by Alkemade (10), it is apparent that this nebulization principle offers great promise as an approach to sample introduction in flame spectrochemical analysis.

A major difference between the Babington nebulization technique and the conventional capillary pneumatic nebulizer arises from the fact that the conventional nebulizer requires the sample to pass through a small ($\approx$ 0.36 mm) capillary orifice. In contrast, the Babington nebulizer requires that only _gases_ pass through an orifice; the relatively unrestricted (2.38 mm) _sample_ flow of this system provides the basis for high solids sampling and represents

the primary advantage of Babington nebulization as applied to spectrochemical analysis. The upper limit on salt and solids content as well as viscosity of a slurry that may be directly sampled by this technique is determined by the ability of the material to pass through a pumping system. This paper deals with the application of a specially developed nebulizer based on the Babington principle in combination with high solids slot burners to provide direct atomic absorption analysis of highly complex environmental, clinical, and food samples.

EXPERIMENTAL

Apparatus. A single channel, single beam atomic absorption spectrometer similar to most late model commercial designs was constructed with readout in analog and digital form. Both absorbance and %T modes are provided.

Optical components included Jarrell Ash (Waltham, Mass.) and Varian Techtron (Springvale, Vic., Australia) hollow cathode lamps (Cd, Cu, Zn, Fe, and H_2), a 1.5 meter combination optical rail and bench, a Princeton Applied Research (Princeton, N. J.) optical chopper operating at 312 Hz, Modern Optics (El Monte, Calif.) 150 mm focal length, 51 mm diameter, and 25 mm focal length, 25 mm diameter convex fused silica external intermediate and slit imaging lenses, Heath (Benton Harbor, Mich.) 0.35 meter, f/6.8 monochromater with 250 nm blazed grating (first order), and a Hammamatsu (Middlesex, N. J.) R212 UH photomultiplier tube. The external optics are positioned to produce hollow cathode images (@ 250 nm) of magnification (1.0) at the center of the slot burner and of reduced magnification (0.125) at the

entrance slit of the monochromater.

Electronic components included hollow cathode and photomultiplier
power supplies, photo current pre-amplifier, lock-in amplifier, logarithmic
amplifier, Data Technology Corp. (Woburn, Mass.) 343 digital volt meter,
and Bausch & Lomb (Rochester, N. Y.) 100 mv VOM-5 strip chart recorder.
A standard FET input photocurrent preamplifier circuit with variable gain,
variable time constant, and current offset was constructed using a
Burr Brown (Tucson, Ariz.) 3522L integrated circuit operational amplifier
as the basic component. A lock-in amplifier circuit similar in design to
that of Horlick (11) utilized in the referenceless mode with addition of
variable damping was constructed using a Signetics (Sunnyvale, Calif.)
561 phase locked loop, 741 operational amplifiers, and a Teledyne Semicon-
ductor (Mountain View, Calif.) LM208 drift stabilized operational amplifier
in the demodulation section as the principle components. The logarithmic
amplifier was designed employing an Analog Devices (Norwood, Mass.) 752N
temperature compensated logarithmic feedback element and a Signetics 536
operational amplifier according to the suggested circuit supplied by Analog
Devices for logarithmic voltage conversion. Overall calibrated readout
scales of 0-100% T, 0-2 A, 0-1 A, 0-0.5 A, 0-0.2 A, and 0-0.1 A are provided.
The optical and electronic design is generally similar to that of several
late model standard commercial instruments.

A high solids single slot air-acetylene burner head similar in design
(except for the wider 0.81 mm x 10 cm. slot used in this study) to the
standard 0.51 mm x 10 cm. slot air-acetylene head sold by Varian Instruments,
an Instrumentation Laboratory (Lexington, Mass.) CAT. NO. 24036-03 commercial

"High Solids" 0.81 mm x 5 cm. single slot N_2O-acetylene burner head, and a Jarrell Ash "Tri flame" 10 cm. air-acetylene head were used in these investigations. The two high solids burner heads were found to be desirable for salt, sugar, and solids contents in excess of 5% to prevent clogging and gumming of the slot. Flashback has not occurred to date in the modified high solids air-acetylene design, and the high solids N_2O head sold by Instrumentation Laboratories flashes back only if proper flow rates and flame stoichiometries are not maintained during light-up, operation, and shut-down.

Provision was made at the entrance to the premix chamber for a quick interchange connection allowing press-fit installation of a Varian Techtron variable aspiration rate conventional pneumatic nebulizer with externally adjustable glass bead impactor as well as connection to the modified Babington nebulizer. The smallest restriction in the 29 mm i.d., 48 cm. path aerosol refinement and premix chamber is the 15.9 mm flow spoiling restriction. The modified Babington nebulizer (Figure I) is housed in a 55 mm i.d., 67 mm o.d., cylindrical plexiglass chamber which is connected to the premix chamber by means of a 33 mm i.d. flexible plastic hose. A 10 mm i.d. exit drain is provided for excess sample and large particle runoff. Nebulizer inserts are held in place by a compression fitting elbow. The nebulizer utilizes a polished 6 mm. o.d., 5.5 mm i.d. closed, rounded end, metal tube with a single 0.61 mm orifice located 3 mm below the end of the tube. The 3 mm spherical impactor is mounted on a translational slide to provide gap adjustment externally during aerosol production and flame atomization (optimal gap ~ 1.4 mm). Sample delivery is accomplished

by a Manostat (New York, N. Y.) 72 895-10 peristaltic pump with head and
rollers modified to accept 2.38 mm i.d. Tygon tubing. An acceptable sub-
stitute pump that could be used without modification would be Cole Parmer-
Masterflex (Chicago, Ill.) 7016 pumphead, 7545-10 variable speed pump drive,
and 6408-02 tubing or any equivalent of this suggested pumping system
capable of delivering a steady flow rate of 20 - 25 ml/min.

Sample is pumped from the tube (located 1 mm above the nebulizer) over
the surface of the nebulizer insert forming a film which is interrupted at
the point of the orifice by the high velocity exit of oxidant gas. This
process serves to generate the aerosol which is then impacted against the
small plastic sphere for additional fragmentation of larger droplets.
Extremely large un-nebulizable particles simply fall away from the insert
and are eventually washed down the drain without having clogged the system.
An Eppendorf (Brinkmann Instruments, Westbury, N. Y.) 1000 microliter syringe
was used to pipet samples conveniently into a glass funnel (60 mm o.d. cone,
6 mm o.d. stem) which is pressed over the input end of the peristaltic
pump tubing.

Procedure. Spectral bandwidths between 0.3 nm and 0.6 nm were used for
all measurements. Cd, Cu, Zn, and Fe resonance lines at 228.8 nm,
324.7 nm, 213.9 nm, and 248.3 nm respectively were used for atomic
absorption measurements. Non-atomic absorption measurements were made
where necessary using a H_2 continuum hollow cathode. The non-atomic
absorbance measurements at 324.7 nm were not affected by the presence of
copper at this spectral bandwidth if the solution concentration was
less than 100 ppm Cu. All samples were far below this level in the

solutions presented to the instrument. The photomultiplier tube was operated at 700 V and, following careful alignment techniques to insure both beams traversed the same flame profile region, hollow cathode current as well as pre-amplifier gain adjustments were made to match the observed relative emission signal intensity of the continuum source to that of the individual hollow cathodes. A check of the non-atomic absorbance was also made without changing lamps (or alignment) using a non-absorbing line at 210 nm emitted from the Zn hollow cathode. Non-atomic absorbance did not exceed 0.01 absorbance units for all samples tested except the 50% $CaCl_2$ sample for which a value of 0.2 A was not exceeded in air-acetylene. Analytically observed flame regions occurred with the center of the beam 6 mm above the burner head.

All direct Babington analyses (with exception of the NBS standard reference material which required dilution of the high levels of Cu and Zn present) were made by the method of minimal dilution standard additions using sample volumes of 1 ml and addition volumes of 10 microliters to avoid loss of concentration sensitivity and to demonstrate that these complex sample types can be run in "no-clog" fashion without dilution. Comparison analyses made using the standard Varian nebulizer were carried out following standard (2) dry ashing, hot mineral acid digestion of the ash, and final dilution to volume with deionized distilled water. A sample of NBS Orchard Leaves (SRM 1571) was also prepared by this process as a check on the ashing and digestion procedure. In the case of Zn, some of the high concentrations reported were determined without dilution in the Babington nebulizer by sensitivity reduction through shortened path length accomplished by rotation

of the slot burner head.

The nebulizer is optimally driven at an oxidant pressure of 50 - 80 psi. for spectrochemical analysis to yield flow rates between 9 and 12 lpm. The pressure drop occurs across the nebulizer orifice so normal drain and trap collection procedures may be used for excess sample runoff. The peristaltic pump is normally operated at 20 - 25 ml/min. 1 ml samples are pipetted, using an Eppendorf (or similar) microsyringe, into the glass cone yielding a transient signal at the recorder. Larger samples may be used to produce a steady state signal at the readout if desired, but 1 ml is sufficient to give a transient signal of similar concentration sensitivity and precision. The smaller volume transient sampling method greatly reduces problems associated with burner slot clogging. This transient method of sampling is similar to that discussed for conventional nebulizers by Sebastiani et al. (12), by Manning (13), and by Berndt and Jackwerth (14) except that the sample size is somewhat larger in the high solids Babington system.

RESULTS AND DISCUSSION

Improved Nebulizer Design. Initial evaluation of the "Hydrosphere" respiratory Babington nebulizer for use in flame analysis demonstrated its ability to produce stable aerosols yielding reasonable spectrochemical sensitivity. This was achieved utilizing gas flow rates compatible with the normal values (8 - 12 lpm) employed for oxidant gases in conventional atomic absorption burners. Air-acetylene, nitrous oxide-acetylene, and argon-hydrogen-entrained-air flames were all supported adequately by this system. Unfortunately the large solution reservoir and large-scale design of the commercial glass respiratory nebulizer required prohibitively large sample sizes in excess

of 500 ml. Subsequent investigations eventually led to development of an improved design involving peristaltic pump sample delivery to the scaled down, geometrically improved metal version of the Babington nebulizer shown in Figure I. These modifications led to sample sizes of 1 ml making the Babington nebulization principle reasonably applicable for the first time to routine spectrochemical sampling.

Instrument and Nebulizer Performance. Table I summarizes the performance of the improved Babington nebulizer in comparison with several conventional capillary pneumatic nebulizers commonly used for atomic absorption spectrometry. The parameter used for comparison was sensitivity (concentration required to produce 1% absorption) of cadmium measurement at 228.8 nm in a 10 cm. air-acetylene flame. Table I demonstrates that the observed sensitivities for the commercial capillary pneumatic nebulizers tested in the instrument constructed for these studies are essentially no different from the values advertised by the manufacturers for the individual nebulizers operating in the corresponding commercial instruments. This indicates that the instrument constructed for these investigations performs at state-of-the-art levels and represents a valid system for nebulizer evaluation.

The data indicate some performance differences between major brands of conventional pneumatic nebulizer, however the entire range of performance spans only a factor of 2.4 indicating similar aerosol production for the commercially available models of capillary pneumatic nebulizer evaluated in this study. The observed sensitivity for the Babington nebulizer is 0.014 ppm Cd (Table I) which falls well within the same performance range as the

commercial pneumatic nebulizers. These results confirm the predicted applicability of the Babington principle to sample introduction for spectrochemical analysis. Although the present "high solids" design of Babington nebulizer requires more sample (1 ml) than the conventional pneumatic nebulizer (0.2 ml) for high sensitivity transient sampling, the conventional device is rapidly clogged by high solids samples such as whole blood, tomato sauce, etc. These difficult matrices are however readily nebulized by the improved Babington technique. The results summarized in Table I have indicated that this is accomplished without sacrifice in sensitivity (compared with the commercially available pneumatic nebulizers).

Analysis of High Solids Samples. Direct Zn and Cu analyses in air-acetylene of several highly complex samples by the Babington procedure are summarized in Table II. This sample group includes those matrices where the metal is contained entirely in soluble form. A digestion was done on an aliquot of each sample to provide the comparison (conventional nebulizer) analyses listed opposite the Babington results in Table II. Good agreement (within the limits of sample homogeneity) between the procedures is demonstrated by Table II. This indicates the clear feasibility of applying the Babington technique to direct spectrochemical analysis of untreated (except for solids such as the NBS leaf tissue) samples and slurries of increased viscosity, high suspended solids content, and elevated salt content. Salt contents as high as 50% (w/v) or greater are readily accommodated if the solubility is this high. It should be noted that, for quantities $\geq$ 1 g of solid sample

to be digested, nebulizer tolerance of higher salt contents allows less dilution of the final digest. This results in a higher signal at the instrument and an overall sensitivity improvement on the basis of the original solid sample.

Effect of Suspended Particulate Size. Additional sample categories are given in Table III. Comparison analyses in part 1) show that the Babington nebulizer is not affected by the large metal containing pulpy particles found in samples such as tomato sauce. The soluble metal content is determined correctly without sample clogging. Large pulpy particles are simply washed away from the nebulizer insert and removed via the drain by the flowing sample stream. No measurable memory effects are encountered if a portion of distilled water is nebulized between samples. In contrast to the large sized particulate case, part 2) of Table III demonstrates that the direct Babington spectrochemical response to sample suspensions of small metal containing particles (such as milk solids) agrees with the total metal (solids + solution) analysis when the method of additions is employed. The fact that this occurs even though the "add" is made entirely in soluble form substantiates the premise that the smaller milk solid particles are delivered to the burner in a percentage similar to solution droplets thus yielding a total metal response. The samples in parts 1) and 2) of the table represent particle size extremes for which the Babington procedure agrees with either the total metal or soluble metal content of the sample rather than giving an intermediate response.

The case of intermediate sized suspended particles is summarized in the comparison analyses of part 3) of Table III. Zn and Fe occur in blood plasma

(soluble form), but are present in much higher levels in red blood cells. The table indicates that the Babington procedure is measuring a combination of plasma and red cell content of Zn and Fe in fresh (un-hemolyzed) whole blood because the direct Babington result is much higher than the value measured by conventional digestive analysis for plasma alone. The direct Babington results (Zn, Fe) however fall short of the total Zn and Fe content as measured by digestion procedures. This is readily explained by the larger size (5 - 9 microns) of intact red blood cells in comparison to the median mass diameter (3.6 microns) of solution aerosol droplets produced by the Babington nebulizer. Aerosol refinement processes in the premix chamber undoubtedly cause these larger cells to be delivered to the burner in a lesser percentage (due to their size and weight) than the droplets produced from blood plasma and the soluble "standard add". This results in a lowered measurement not corrected for by the method of additions since the aqueous "add" does not undergo the same percentage droplet selection process in the pre-mix chamber as the red cell metal.

Copper represents a different situation in fresh blood than iron and zinc, because the copper in blood is present primarily in soluble plasma form. Table III, 3) demonstrates that the Babington nebulizer yields a direct atomic absorption response that is correct in this case even though the sample has not undergone hemolysis (cell rupture).

The Zn result for hemolyzed whole blood (Table II) demonstrates that simple hemolysis facilitates a correct Babington measurement of total Zn content. Hemolysis may be easily induced by standard freeze-thaw, sonification, or osmotic rupture procedures. Elements not contained appreciably by the red cells (such as Cu) can be determined directly in

plasma or whole blood without treatment. If metal content of plasma or serum is desired (as is often the case) rather than whole blood, then it is _not_ desirable to induce or allow hemolysis to occur especially for elements such as Zn and Fe. In this case, the plasma or serum should be separated as is normally done in conventional analysis, but it may now be analyzed directly by the Babington procedure without further treatment.

Matrix Effects Correctable by the Method of Additions. Although samples of variable viscosity, salt content, and solids content are readily analyzed by the standard addition Babington procedure, these properties may affect the calibration through surface tension and viscosity effects in the nebulizer, variable aerosol refinement in the premix chamber, as well as vaporization and diffusion effects in the flame. No attempt was made to identify the individual contributing sources of the collective matrix effect; it was simply calibrated by the method of additions for all analyses made.

CONCLUSIONS

The overall observations of these investigations are that the modified Babington nebulizer method of sample introduction into flame systems represents a rapid and reliable method of high solids atomization when suspended particle size is taken into consideration, standard addition procedures are utilized, and normal burner-nebulizer sensitivity for a 1 ml sample is adequate for the samples to be analyzed. Untreated samples and slurries containing large quantities of dissolved sugar and salt as well as suspended solids are analyzed directly with only moderate matrix effects that are easily compensated for in a high solids burner system. The unrestricted flow-through nebulizer design provides a system that is convenient to operate and is relatively "clog-free" without any sacrifice in concentration sensitivity. The authors believe that these studies represent the first reported application of the Babington principle of nebulization to spectrochemical analysis.

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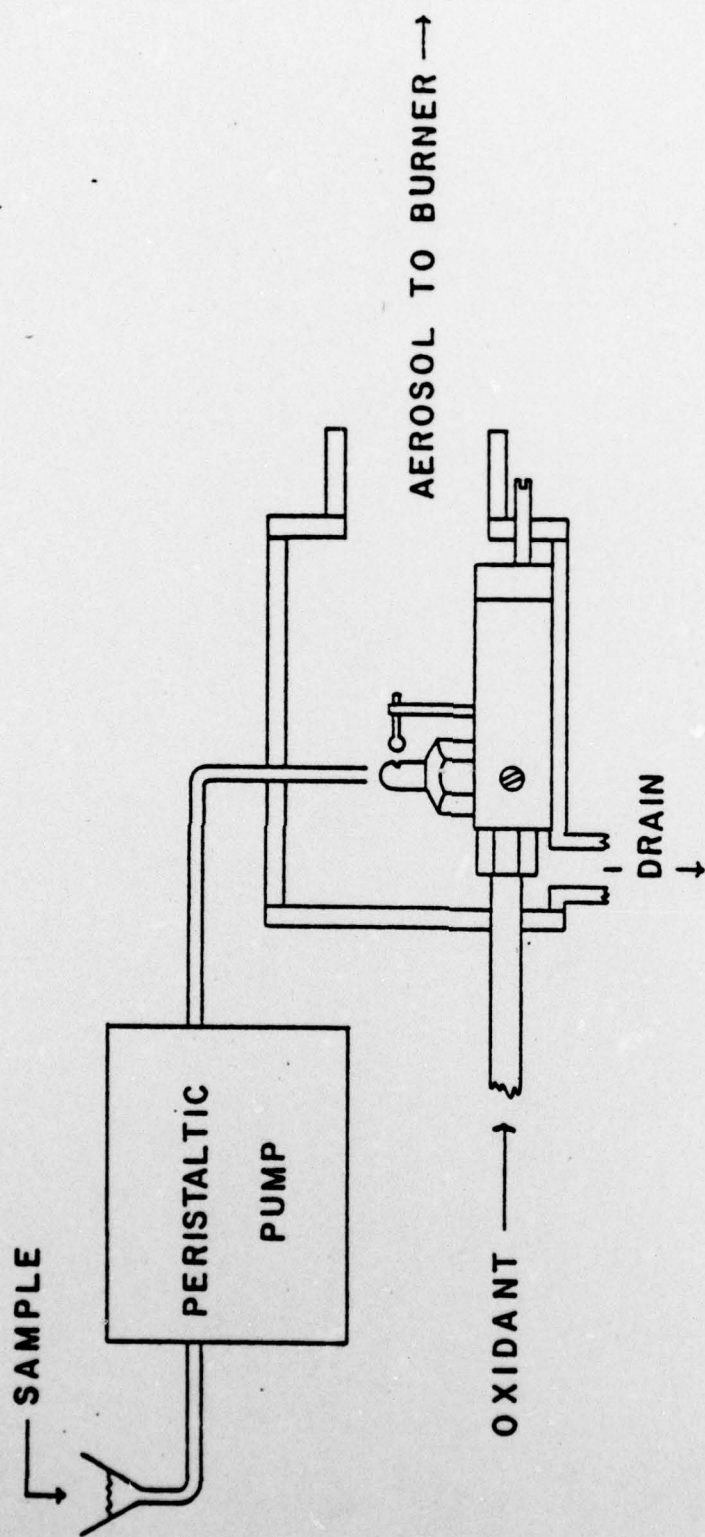Figure I. New high solids nebulizer (Babington principle).

TABLE I. Nebulizer Sensitivities in Air-Acetylene at $Cd_{228.8}$ nm

Nebulizer	Observed Sensitivity	Manufacturers Listed Sensitivity (in the commercial instrument)
Modified Babington Nebulizer	0.014 ppm	----
Varian Techtron Adjustable Pneumatic Nebulizer	0.010 ppm	0.011 ppm
Jarrell Ash 810 Pneumatic Nebulizer	0.018 ppm	0.020 ppm
Jarrell Ash Hetco Pneumatic Nebulizer	0.022 ppm	(0.024 – 0.040 ppm)[a]
Perkin Elmer Pneumatic Nebulizer	----	0.025 ppm
Beckman 495 Premix Pneumatic Nebulizer	----	0.015 ppm

[a] Based on a private communication with Jarrell Ash personnel.

TABLE II. Analysis of High Solids Samples

Sample	Zn (ppm)		Cu (ppm)	
	Direct Babington Analysis	Conventional Analysis (Digest) (Varian Nebulizer)	Direct Babington Analysis	Conventional Analysis (Digest) (Varian Nebulizer)
Hemolyzed Whole Blood	12.	13.	0.63	0.61
Urine	0.63	0.67	0.062	0.065
Sea Water	< 0.021	< 0.014	0.063	0.069
NBS Orchard Leaves[a] (digest)	24.	27.	13.	11.

[a]NBS certified value: 25 ± 3 ppm Zn and 12 ± 1 ppm Cu for the Orchard Leaves SRM 1571.

TABLE III. Particle Size Effects

Sample	Zn (ppm)			Cu (ppm)			Fe (ppm)		
	Babington[a]	Total[b]	Soluble[c]	Babington	Total	Soluble	Babington	Total	Soluble
1) Hunt's Tomato Sauce (Suspended particulate size in low millimeter range)	0.62	1.8	0.64	0.55	1.7	0.53	----	----	----
2) Carnation Evaporated Milk Concentrate (Suspended particulate size < 5 microns)	7.5	7.9	1.6	0.17	0.17	0.11	----	----	----
3) Untreated (Babington only) Whole Blood (Suspended particulate size 5 - 9 microns)	3.9	7.5	0.73	0.69	0.71	0.69	240.	520.	1.5

[a] Untreated whole sample. [b] Digested whole sample. [c] Digested supernatant from centrifuged sample.